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THE SPECTROSCOPY AND REACTION KINETICS OF
COORDINATIVELY UNSATURATED META. (U) NORTHWESTERN UNIV
EVANSTON IL DEPT OF CHEMISTRY E WEITZ 24 OCT 87

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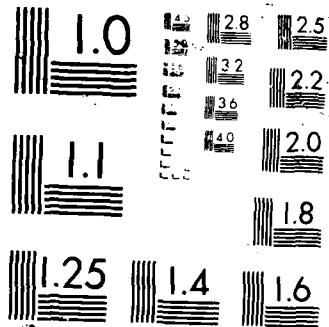
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A program involving the investigation and characterization of reactions of coordinatively unsaturated organometallic species is described. The program emphasizes the measurement of rates of reaction of photolytically produced coordinatively unsaturated species with the parent and rates for cluster formation. Experimental measurements are performed using a time resolved transient absorption apparatus which uses a line tunable CO ₂ laser and a diode laser to record spectral and kinetic information by means of probing absorptions in the CO stretch region of the infrared. Systems that have been investigated include coordinatively unsaturated species generated from the Fe(CO) ₅ , Cr(CO) ₆ and Mn ₂ (CO) ₁₀ parents. The results of experiments with these systems are discussed.			
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The Spectroscopy and Reaction Kinetics of
Coordinatively Unsaturated Metal Carbonyls
Contract #AFOSR-83-0372

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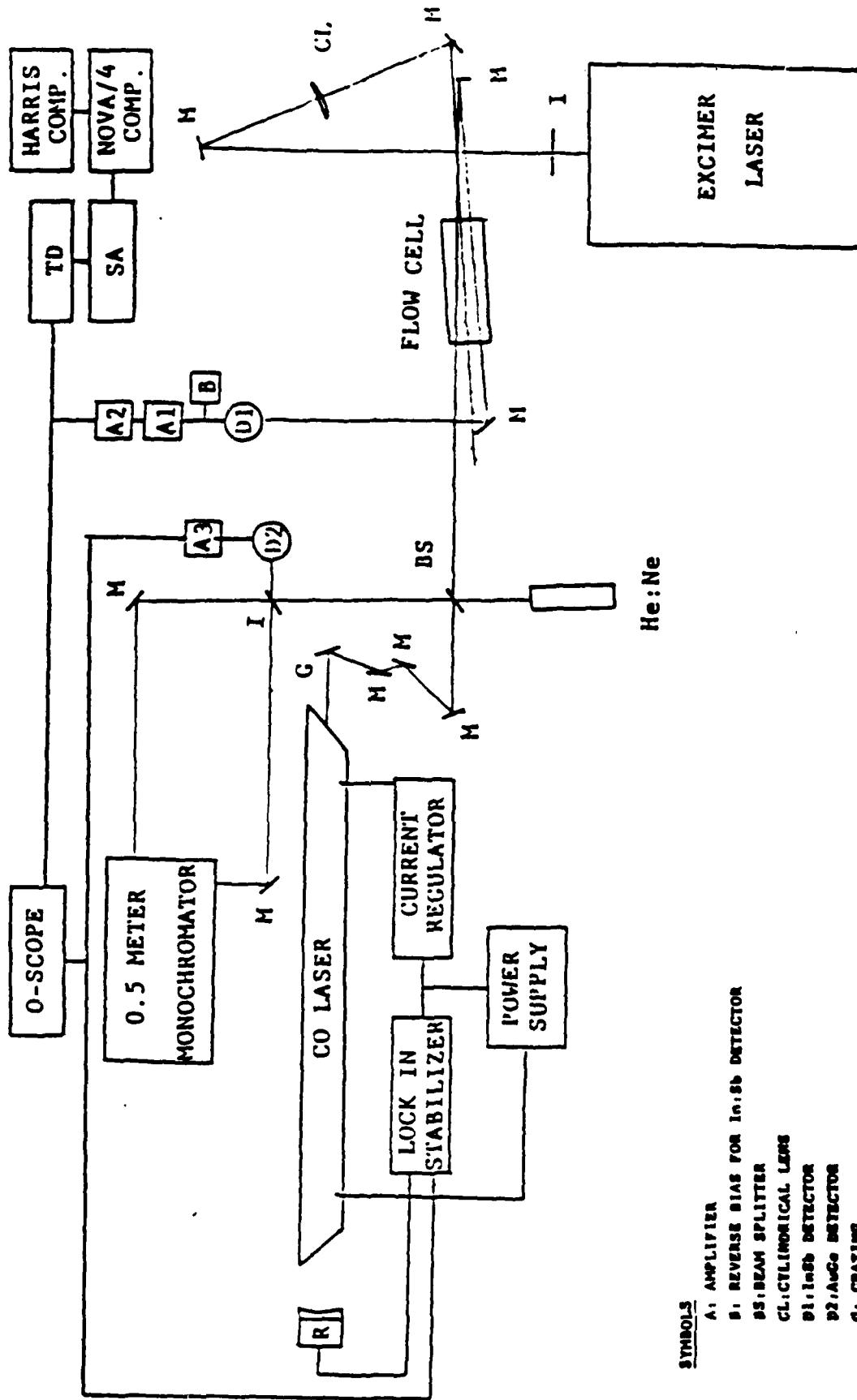
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Coordinatively unsaturated metals are important chemical species with a variety of interesting and unique chemical properties. These species have been shown to be exceedingly reactive. They are important catalysts, reaction intermediates and can form oligomers and metal clusters containing multiple metal centers.¹ Despite their importance and a great deal of interest in this area, little is known regarding details of the structure or reactivity of coordinatively unsaturated metals. Their extreme reactivity has heretofore been an impediment to detailed study of these species in the liquid phase and has virtually precluded study in the gas phase. Until recently nothing was known about the mechanism or kinetics for reactions or cluster formation in these systems.

In an effort to alter that situation we developed an apparatus and a technique which allows us to study coordinatively unsaturated metals in either phase in real time.^{2,3} The use of transient absorption spectroscopy has allowed us to detect and monitor coordinatively unsaturated metals. Though our work is now well summarized in a number of review articles,⁴⁻⁶ a summary will be presented here for convenience. Most of our studies, to date, have involved excimer laser photolysis of volatile metal carbonyls to yield gas phase

Figure 1

DIAGRAM OF APPARATUS USED FOR MEASUREMENT OF TRANSIENT ABSORPTIONS



SYMBOLS

- A₁**: AMPLIFIER
- B₁**: REVERSE BIAS FOR In:Sb DETECTOR
- BS**: BEAM SPLITTER
- CL**: CYLINDRICAL LENS
- D₁**: LEDS DETECTOR
- D₂**: D2-AUGA DETECTOR
- G₁**: GRATING
- I**: IRIS
- M**: MIRROR
- SA**: SIGNAL AVERAGER
- TD**: TRANSIENT DIGITIZER

coordinatively unsaturated metal carbonyls or metal atoms. Most of our work has employed an apparatus that uses a line tunable CO laser, as a probe, to monitor the change in absorption of the sample following the excimer laser photolysis pulse. However, we have now integrated a cw diode laser into the apparatus. This allows us to probe transient species in any region of the infrared and thus vastly increase the versatility of the apparatus. A diagram of this apparatus is shown in Figure 1. Though the diagram depicts a CO laser, the apparatus is set up so the probe laser can also be a diode laser.

To actually generate a transient spectrum the change in absorption of the probe laser is monitored at a variety of different laser frequencies with the time versus absorbance signal digitized via a transient digitizer which feeds the data to a signal averager from which it is fed to a computer. The computer takes all the frequency dependent data and assembles it into a transient absorption spectrum which can be displayed as a function of time following the photolysis pulse. A typical transient absorption spectrum is shown in Figure 2 which has been taken from reference 5. Features in a transient absorption

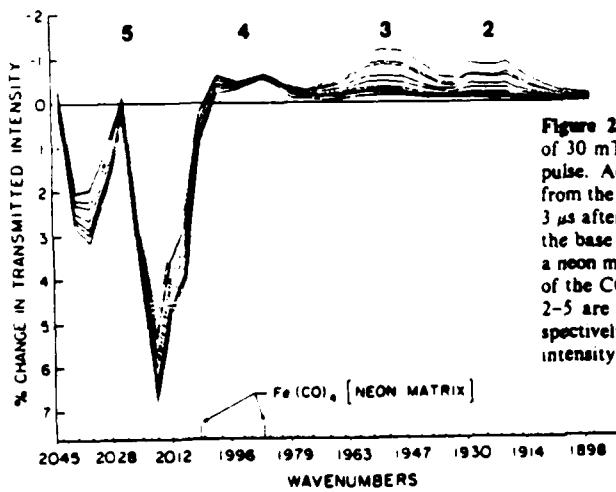


Figure 2. Portion of the infrared spectrum shown following photolysis of 30 mTorr of $\text{Fe}(\text{CO})_5$ in 5 Torr of argon with a KrF excimer laser pulse. Adjacent traces are taken at 3- μs intervals. The largest excursion from the base line for features 2-4 is the first trace with that trace taken 3 μs after the excimer laser pulse. Nine traces are shown in addition to the base line. Also shown is the position of the $\text{Fe}(\text{CO})_5$ absorption in a neon matrix. The tic marks above the abscissa indicate the frequencies of the CO laser lines that were used to construct the traces. Features 2-5 are $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_4$, and $\text{Fe}(\text{CO})_3$ absorptions, respectively. Percent change in transmitted intensity refers to CO laser intensity.

spectrum can be identified by a procedure we call a "kinetic bootstrap" procedure.⁵ In this procedure an excess of the ligand or ligands that are lost

in photolysis is added to the sample mixture. On photolysis we can then watch a coordinatively unsaturated compound react with added ligand to generate successively less coordinatively unsaturated species and finally parent. As a specific example, on ArF photolysis of $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ are formed.⁷ When these are formed in the presence of added CO we observe that $\text{Fe}(\text{CO})_2$ reacts with CO to form more $\text{Fe}(\text{CO})_3$ which reacts with CO to form $\text{Fe}(\text{CO})_4$ which also reacts with CO to form $\text{Fe}(\text{CO})_5$. Since these reactions are sequential each reaction product can be clearly identified. An example of this procedure is shown in figure 3 which has been taken from reference 5, where

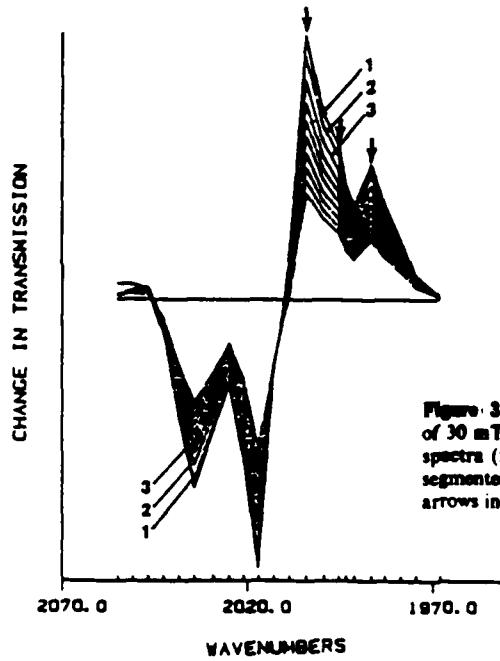


Figure 3. Transient absorption spectrum generated on KrF photolysis of 30 mTorr of $\text{Fe}(\text{CO})_4$ with 100 Torr of CO. The figure depicts the spectra (from ~ 2060 to 1970 cm^{-1}) over a 5-μs range which has been segmented into ten equal time intervals. The first three are marked. The arrows indicated the partially resolved A₁, B₁, and B₂ bands of $\text{Fe}(\text{CO})_4$.

$\text{Fe}(\text{CO})_4$ is seen reacting with CO to form $\text{Fe}(\text{CO})_5$.⁷ Note the isobestic point indicating a clean A \rightarrow B reaction. Once features in the transient absorption spectrum are identified, a specific feature can be monitored as a function of time and its kinetic behavior discerned. Our current apparatus has a time response of 30 nsec, a frequency range of 350-2350 and 2900-3300 cm^{-1} , and a

typical detection sensitivity corresponding to 10^{10} coordinatively unsaturated metal carbonyl molecules.

With the above technique, we have been able to obtain the first gas phase infrared spectrum of a coordinatively unsaturated metal.^{2,3} We have obtained infrared spectra in the CO stretch region for the species $\text{Fe}(\text{CO})_x$ ($x = 2, 3, 4$) and have measured the rate of reaction of $\text{Fe}(\text{CO})_x$ with CO and the activation energies for these reactions.⁷ Data for reaction of $\text{Fe}(\text{CO})_3$ and the other $\text{Fe}(\text{CO})_x$ species is presented in Table 1.

Table 1. Summary of the Bimolecular Rate Constants for $\text{M}(\text{CO})_x\text{-CO}$

Recombination Reaction

	spin allowed	gas-phase rate constant, $10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$
$\text{Fe}(\text{CO})_4 + \text{CO} \rightarrow \text{Fe}(\text{CO})_5$	N	0.003
$\text{Fe}(\text{CO})_3 + \text{CO} \rightarrow \text{Fe}(\text{CO})_4$	Y	1.2
$\text{Fe}(\text{CO})_2 + \text{CO} \rightarrow \text{Fe}(\text{CO})_3$	Y	1.7
$\text{Cr}(\text{CO})_5 + \text{CO} \rightarrow \text{Cr}(\text{CO})_6$	Y	1.5
$\text{Cr}(\text{CO})_4 + \text{CO} \rightarrow \text{Cr}(\text{CO})_5$	Y	2.4
$\text{Cr}(\text{CO})_3 + \text{CO} \rightarrow \text{Cr}(\text{CO})_4$	Y	1.8

It is interesting to note that the reaction of $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ with CO are of similar magnitude while the reaction of $\text{Fe}(\text{CO})_4$ with CO is slower by almost three orders of magnitude. The fact that the reaction of $\text{Fe}(\text{CO})_4$ with CO is anomalously slow relative to typical addition reactions of coordinatively unsaturated species is confirmed by studies on the $\text{Cr}(\text{CO})_6$ ^{8,9} and $\text{Co}(\text{CO})(\text{NO})_3$ ¹⁰ system. So the question arises, why is this reaction different from all these other reactions? The answer to this question can be found in studies of the electronic structure of $\text{Fe}(\text{CO})_4$. The ground state of $\text{Fe}(\text{CO})_4$ is a triplet.¹¹

Thus the addition reaction of CO to $\text{Fe}(\text{CO})_4$ is spin forbidden. This has further implications for the $\text{Fe}(\text{CO})_x$ system. If a spin forbidden reaction is expected to be significantly slower than a spin conserving reaction, then the ground states of $\text{Fe}(\text{CO})_3$ ¹² and $\text{Fe}(\text{CO})_2$ are also triplets. This prediction has been previously made for $\text{Fe}(\text{CO})_3$ and we have postulated, based on our kinetic data, that $\text{Fe}(\text{CO})_2$ has a triplet ground state.

We find that only one of two isomers of $\text{Fe}_2(\text{CO})_8$ ¹³ forms on reaction of $\text{Fe}(\text{CO})_3$ with $\text{Fe}(\text{CO})_5$.²⁰ We believe this situation occurs because the kinetics of reaction of $\text{Fe}(\text{CO})_3$ with $\text{Fe}(\text{CO})_5$ is spin controlled. We are working to verify this hypothesis which could have important ramifications for understanding and predicting which clustering reactions will occur in the gas phase.

We have performed similar studies for the $\text{Cr}(\text{CO})_6$ system, obtaining spectra for $\text{Cr}(\text{CO})_x$ ($x = 2, 3, 4, 5$)^{8,9} and have measured rates of reactions of $\text{Cr}(\text{CO})_5$ with CO, CH₄, N₂, H₂ and C₆H₆.¹⁸ Data for the reaction of $\text{Cr}(\text{CO})_x$ with CO are also presented in Table 1. We have also observed a heretofore unreported clustering process in the $\text{Cr}(\text{CO})_x$ system.⁹ We find that all the $\text{Cr}(\text{CO})_x$ fragments react readily with parent. In particular, we have investigated in detail the clustering process for the reaction of $\text{Cr}(\text{CO})_4$ and $\text{Cr}(\text{CO})_5$ with parent. We find that both reactions occur at a rate that is within a factor of two of gas kinetics.⁹ We assign the species initially produced via these clustering reactions to $\text{Cr}_2(\text{CO})_{10}$ and $\text{Cr}_2(\text{CO})_{11}$, respectively, and have recorded the first gas phase spectra for these species in the carbonyl stretch region.⁹

We have also obtained results on the $\text{Mn}_2(\text{CO})_{10}$ system.^{15,16} As with $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$, we have recorded the spectra of the photofragments identified following photolysis at 193, 249 and 351 nm.¹⁶ Both $\text{Mn}(\text{CO})_5$ and

$\text{Mn}_2(\text{CO})_9$ are observed with a wavelength dependence favoring the initial photochemical step leading to production of $\text{Mn}_2(\text{CO})_9$ as a function of increasing photolysis energy. $\text{Mn}(\text{CO})_5$ has been observed to undergo radical-radical recombination to form $\text{Mn}_2(\text{CO})_{10}$ with a rate constant that is near gas kinetic. $\text{Mn}_2(\text{CO})_9$ has been observed to react with CO to reform $\text{Mn}_2(\text{CO})_{10}$ with a rate constant that is equal to $(2.4 \pm 0.8) \times 10^6$ 1 mole⁻¹ s⁻¹. Both of these results are compatible with kinetic results in solution.¹⁷

Other interesting features of results in this system are the observation of photolysis products in addition to $\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_9$. Other absorptions are observed which increase in number and intensity as the photolysis wavelength is decreased. Though these results should still be considered as preliminary, these additional photoproducts are likely to be dissociation products of $\text{Mn}(\text{CO})_5$ rather than $\text{Mn}_2(\text{CO})_9$. This conclusion was reached by studies of the time evolution of various absorption bands on addition of CO to the system.¹⁸ Thus the major additional photoproducts are $\text{Mn}(\text{CO})_x$ where $x < 5$. This result is compatible with the hypothesis first put forth by Vaida that the Mn-Mn bond strength increases as additional CO's are lost from $\text{Mn}_2(\text{CO})_9$.¹⁹

There have also been some very interesting results in the area of photochemistry and photophysics. For example, a general feature in the production of coordinatively unsaturated metal carbonyls in the gas phase is that they are typically formed with internal excitation.⁵ As the internal excitation relaxes the absorptions narrow and shift toward higher frequency. This behavior has been observed in all metal carbonyl systems studied to date with an increasing degree of excitation observed in a given photofragment as the energy of the photolysis photon increases.

Another interesting observation regarding the dissociation process is a general increase in the degree of unsaturation of the photoproducts as a

function of the energy of the input photon.⁵ This behavior is apparent in either the iron or chromium system where the branching ratios for photoproducts changes dramatically with input energy and is also observed in the Mn₂(CO)₁₀ system. Almost exclusively Fe(CO)₄ is formed for XeF laser photolysis while for KrF laser photolysis the product mix shifts toward Fe(CO)₃. For ArF laser photolysis almost exclusively Fe(CO)₂ is produced. Similar behavior is observed in the chromium system with XeF photolysis producing predominantly Cr(CO)₅, KrF photolysis predominantly Cr(CO)₄ and ArF photolysis a mix of products including Cr(CO)₃ and Cr(CO)₂.

The behavior described in the two preceding paragraphs is compatible with a straightforward mechanism for photodissociation which also reconciles observed differences in product distributions in the gas phase versus condensed phases.⁵ The initially absorbed photon initiates a photochemical event which results in loss of a CO ligand and the production of a photofragment which is highly internally excited. This excited molecule is rapidly relaxed in condensed phase due to the high density of surrounding collision partners. Thus the net result of photolysis in these and related systems in condensed phase is loss of one ligand. However, in the gas phase additional processes can occur. The energized photofragment can go on to further dissociate in an RRKM like process leading to multiple products. Dissociative steps are terminated when the excited molecule can be collisionally stabilized on the timescale of the next possible dissociative event.

We have also obtained information on the spectroscopy and thus structure of the photofragments produced in photolysis of the iron, chromium and manganese carbonyls. Virtually all of the gas phase absorption features that we have observed for coordinatively unsaturated compounds of Fe, Cr and Mn are compatible with their reported matrix structures.^{4,5} This is an important

observation in that it implies that matrix isolated coordinatively unsaturated metal carbonyls are not subject to "matrix effects" and the structure determined in the matrix is very likely to be that of the gas phase species. Some subtleties may modify this statement such as the effect on the structure of coordinated rare gas molecules or other coordinated matrix or glass substrate molecules. Nevertheless, this statement is likely to be accurate in a large majority of cases. The only possible exception to this statement that we have observed to date, deals with a the difference in position of the semi-bridging CO band in $Mn_2(CO)_{10}$ in the matrix versus the gas phase. This band is observed to be at higher frequency in the matrix which is counter to typical behavior. This could indicate a change in structure in the gas phase versus the matrix for this compound. However, until further studies are completed the previous statement should be regarded more as conjecture than proven fact.

We are also investigating the $Fe(CO)_2(NO)_2$ system where we are primarily interested in determining the relative importance of simple addition reactions versus displacement reactions.²¹ We are probing this question by looking at reactions that occur following photolysis of $Fe(CO)_5$ in a bath of NO molecules. Since $Fe(CO)_2(NO)_2$ is the only stable mixed iron carbonyl nitrosyl, we are investigating how the kinetics and branching ratios for reaction of the various $Fe(CO)_x$ moieties lead to this species. This work is being done by following both the NO and CO absorptions of the parent compound and the coordinatively unsaturated species. Work on this system is not yet conclusive with regard to all of the processes going on in the system. However, we do find that $Fe(CO)_3$ and $Fe(CO)_2$ react very readily with NO while $Fe(CO)_4$ is virtually inert to reaction with NO. Following reaction of $Fe(CO)_3$ with NO we find that the addition complex $Fe(CO)_3NO$ does not seem to react further with NO. However, it seems to have a high propensity for reaction with parent,

presumably leading to a polynuclear metal species of yet unknown structure.

$\text{Fe}(\text{CO})_2\text{NO}$'s reaction kinetics have been less well characterized however, though it does appear that it reacts with NO to generate $\text{Fe}(\text{CO})_2(\text{NO})_2$ but can also react with parent.

Finally, we have been investigating some predictions on relative rates of reaction of metal carbonyls with various ligands which were made by Roald Hoffmann based on an inorganic analog of Woodward-Hoffmann orbital symmetry rules.²² Specifically we have been looking at the reaction of conjugated versus unconjugated dienes with $\text{Fe}(\text{CO})_3$ and $\text{Cr}(\text{CO})_4$.²³ Hoffmann predicted that the former species should react with conjugated dienes faster than with unconjugated dienes and that the latter species should behave in an opposite fashion. These predictions have never been tested because of the prior inability of experimentalists to produce specific coordinatively unsaturated metal carbonyls in a controlled fashion in the gas phase. Obviously these rules for reaction, which have been so important in the understanding of organic reaction kinetics, could also be of paramount importance in predicting rates and pathways of reactions of organometallic species.

We find that the rate of disappearance of the $\text{Fe}(\text{CO})_3$ or the $\text{Cr}(\text{CO})_4$ absorptions on reaction with either conjugated or unconjugated dienes is the same and quite rapid. However, we have indications that in either or both systems what we are looking at is the formation of the first diene - metal bond. This is, we are looking at formation of an η^2 bond. We are still investigating this system to study formation of the second metal-diene bond with the possibility that we can directly observe the unimolecular rearrangement that must occur in these systems for the aforementioned mechanism.

Due to our studies we have formulated a series of propensity rules dealing with the kinetics, structure and photophysics of coordinatively unsaturated metal carbonyls.⁵ They are:

- 1) Addition reactions to coordinatively unsaturated compounds are expected to be significantly faster than substitution reactions.
- 2) Spin conserving reactions of coordinatively unsaturated metal carbonyls are significantly faster than spin disallowed reactions.
- 3) Spin allowed addition reactions of coordinatively unsaturated metal carbonyls with small ligands have been observed to have rate constants near gas kinetic.
- 4) In the gas phase, the degree of coordinative unsaturation increases with increasing photolysis energy.
- 5) Both the coordinatively unsaturated photofragment and the ejected CO tend to be produced with more internal energy as the energy of the photolysis photon increases.
- 6) The nature of the electronic state accessed can influence branching ratios for products. However, within a given electronic state, statements 5 & 6 will prevail.
- 7) The structures of gas phase coordinatively unsaturated metal carbonyls are generally compatible with the structure of the matrix isolated species.

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Gas Phase Photofragmentation of Cr(CO)₆: Time Resolved Infrared Spectrum and Decay Kinetics of 'Naked' Cr(CO)₅.

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J. Am. Chem. Soc., 107, 1432 (1985).

Detection of Transient Organometallic Species by Fast Time-Resolved IR Spectroscopy.

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Photodissociation Pathways and Recombination Kinetics for Gas Phase Mn₂(CO)₁₀

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Studies of Coordinatively Unsaturated Metal Carbonyls in the Gas Phase via Transient, Time Resolved Infrared Spectroscopy

T.A. Seder, A.J. Onderkirk, Stephen P. Church and Eric Weitz
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Studies of Coordinatively Unsaturated Metal Carbonyls in the Gas Phase by Transient Infrared Spectroscopy

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Shedding Light on Organometallic Reactions: The Characterization of Fe(CO)₄, a Prototypical Reaction Intermediate

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S. Gravelle and E. Weitz
To be published.

Reactions of Coordinatively Unsaturated Metal Carbonyls with Conjugated and Unconjugated Dienes
 S. Gravelle, L. van der Burght and E. Weitz
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Kinetics and Mechanisms of $\text{Fe}_2(\text{CO})_8$ Formation in the Gas Phase
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Papers Presented Related to Project

Seminars

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Meetings

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New Methods in Transient Spectroscopy	
American Chemical Society - National Meeting - Chicago	9/85
Symposium on Transient Species	
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